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by

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ABSTRACT

The ability of tri-isobutylphosphine sulphide (TiBPS) to act as an extractant for silver was studied in chlorde and nitrate systems. Emphasis was given to the nitrate system because in the chloride system very little extraction took place under the conditions used. The extractant was able to selectively extract silver in the presence of other metals such as iron, cadmium, lead, copper and zinc. Chemical and spectroscopic analyses of the isolated extracted species showed the following composition: $2TiBPS \cdot AgNO_3$. Sodium thiosulphate was found to be an efficient stripping agent for the silver loaded organic.

EXTRACTION PAR SOLVANT AU SULFURE DE TRI-ISOBUTYLPHOSPHINE (TiBPS) POUR RÉCUPÉRER L'ARGENT CONTENU DANS UN SYSTÈME NITRATÉ

par

G. Pouskouleli et P.J.A. Prud'homme

RÉSUMÉ

On a étudié la capacité du sulfure de tri-isobutylphosphine (TiBPS) d'agir comme produit d'extraction de l'argent à partir des systèmes chlorurés et nitratés. Dans le cadre de ces travaux, on a accordé une importance particulière au système nitraté en raison du faible taux d'extraction obtenu du système chloruré dans les mêmes conditions d'essais. Le produit d'extraction avait une affinité pour l'argent par rapport aux autres métaux tels que le fer, le cadmium, le plomb, le cuivre et le zinc présents en solution. Les résultats des analyses chimiques et spectroscopiques des espèces récupérées isolées ont donné la composition chimique suivante: $2TiBPS \cdot AgNO_3$. Enfin, on a trouvé que le thiosulfate de sodium était un agent d'extraction efficace pour les produits chargés d'argent.

INTRODUCTION

The separation and recovery of silver is mainly achieved by precipitation as silver chloride. This is actually the procedure used for industrial silver recovery. Solvent extraction has been investigated as an alternative to the conventional precipitation process. Thus, different types of extractants such as amines and ammonium salts[1-4], neutral organo-phosphorus compounds (TBP)[5,6], acetylacetone[7], hydroxyquinoline[8], etc. have been used for selective extraction of silver.

Since silver belongs to the soft-metals group[9] it is obvious that sulphur (soft-base) would be more effective in reacting with silver. Therefore, extractants containing sulphur were extensively used for the extraction of silver from different media. Dialkylsulphides[10,11], trialkylthiophosphates[12], dialkylthio and dialkyldithio phosphoric acids[13-16] as well as trialkylphosphine sulphides have been mainly used.

The remarkable selectivity of the thiophosphoryl (P=S) group was first reported in the early sixties[12] and among the compounds having this group the neutral trialkyl phosphine sulphides were described as the most promising[18]. A few studies done with these sulphides, showed very high selectivity for soft metals such as silver, mercury, palladium, etc., from chloride and nitrate systems[17-19]. One of those, the tri-octylphosphine sulphide, has been reported to be used for the separation of noble metals from copper-nickel sludges, on a semi-commercial scale[20].

Tri-isobutylphosphine sulphide (TiBPS) was used in the present investigation for the separation of silver from other metals such as copper, zinc, cadmium, lead and iron in nitrate system. A chloride system was also used but preliminary tests have shown no considerable extraction took place. According to the obtained results TiBPS was found to selectively extract silver by forming a disolvate complex.

EXPERIMENTAL

The extractant (TiBPS), obtained from Cyanamid Canada, was used after recrystallization from methanol as a 3.5 $^{W}/_{o}$ solution in Solvesso 150 (aromatic diluent). TiBPS diluted in Varsol DX-3641 is available under the trade name CYANEX 471 (Cyanamid, Canada).

The aqueous solutions were made up using "chemically pure" grade nitrate salts and their compositions varied as follows (in kg/m^3):

Ag	0.96-1.14	Cu	9.90-10.5
Fe	16.4-20.0	Zn	5.28-5.81
Cd	0.47-0.49	NO_3	77.8-121
Pb	1.00-1.03	pH	1.04-1.05

The extraction tests were carried out in separatory funnels at room temperature. Stripping of the loaded organic was performed with several agents, e.g., HNO_3, NH_4OH, $Na_2S_2O_3$. Analysis of metal values in aqueous and organic phases were performed with AA using standard procedures.

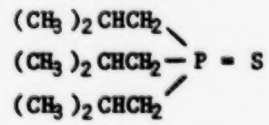
In order to draw information about the extracted species the complex between TiBPS and $AgNO_3$ was synthesized as follows. A solution of TiBPS (0.5 g, 10% excess of the equimolar quantity) in methanol was slowly added to a $AgNO_3$ (0.17 g) solution (30 $^{V}/_{o}$ methanol). The precipitated complex was filtered, washed with water and methanol-water solution and dried to give an off-white crystalline product yield 95%, m.p., 112-113°C. Elemental analysis corresponds to the formula $2TiBPS \cdot AgNO_3$. The complex was soluble in organic diluents and screening the commercial diluents i.e., Solvesso 150, Kerosene, Escaid 110 and Varsol 140, only Solvesso 150 was found to dissolve the complex quickly and to higher concentrations. With the other diluents the dissolution was much slower.

IR spectra were recorded with a Nicolet 6000 FT-IR spectrometer, while a Varian XL-200 spectrometer operating in the pulsed FT mode, was used for the ^{31}P NMR spectra.

RESULTS AND DISCUSSION

Tri-isobutylphosphine sulphide (TiBPS) belongs to a class of extractants in which the sulphur acts as the reaction center during the

extraction. It is therefore expected that silver, a metal of the B-class or soft metal, would react selectively with TiBPS in preference to the other metals of the A-class or hard metals e.g. iron(III), etc.



TiBPS

Our results have indicated that TiBPS extracts silver selectively, not only over hard metals (iron) but also over other soft metals present in the solution, such as cadmium, and over borderline ones such as copper(II), zinc and lead. This selectivity was observed in nitrate systems. When a chloride system was used the selectivity was extended over another borderline metal, bismuth. However, the extraction of silver from a chloride feed solution containing Fe (111 kg/m^3), Cd (0.6 kg/m^3), Pb (5.0 kg/m^3), Cu (11 kg/m^3), Bi (1 kg/m^3), Zn (39 kg/m^3) and Cl^- (269 kg/m^3) was found not to be as good as in the case of nitrate feed. A maximum silver extraction of only 12% was observed with 3 min. contact time. Increase of the contact time up to 10 min. did not improve the extraction. In addition to extraction of silver, iron and copper were also co-extracted at 0.1 and 2.0% levels respectively.

This poor performance of TiBPS as an extractant for silver from chloride media is believed to be due to the presence of silver in the form of several chloride complexes in this highly chloride concentrated solution. Efforts by other researchers to form and isolate a product of AgCl and triphenylphosphine sulphide, $(C_6H_5)_3P{=}S$, were also reported as unsuccessful[21]. Thus, no further work was performed in a chloride system. However, promising results were obtained with the nitrate system and these are presented below.

Kinetic Studies

TiBPS was found to extract silver selectively from a nitrate feed solution, of iron, zinc, copper, cadmium and lead (its composition is given in the experimental section). The reaction kinetics are fast and almost all silver was extracted within a contact time of 2 min. (Table 1). In

practice, a silver extraction of 99% was observed after a contact of 0.5 min. while the other metals were not extracted.

Table 1

Effect of retention time (RT) on distribution coefficient*

pH	RT (min)	D_{Ag}	D_{Cd}	D_{Cu}	D_{Fe}	D_{Pb}	D_{Zn}	% Ag extr.
1.04	0.5	960	0.4×10^{-4}	0.1×10^{-4}	0.2×10^{-3}	0.6×10^{-3}	0.3×10^{-3}	99.89
1.03	1.0	>2000	0.2×10^{-4}	0.6×10^{-4}	0.1×10^{-3}	0.4×10^{-3}	0.3×10^{-3}	99.94
1.04	2.0	>2000	0.4×10^{-4}	0.5×10^{-4}	0.2×10^{-3}	0.4×10^{-3}	0.3×10^{-3}	99.97
1.04	4.0	>2000	0.4×10^{-4}	0.6×10^{-4}	0.2×10^{-3}	0.4×10^{-3}	0.3×10^{-3}	99.97
1.05	8.0	>2000	0.4×10^{-4}	0.5×10^{-4}	0.1×10^{-3}	0.4×10^{-3}	0.3×10^{-3}	99.99
1.05	10.0	>2000	0.4×10^{-4}	0.1×10^{-3}	0.1×10^{-3}	0.5×10^{-3}	0.3×10^{-3}	99.99

*A/O=1, T=24°C

The selectivity of TiBPS for silver over the other metals present, is clearly demonstrated by the separation factors given in Table 2. Thus, these results clearly show that TiBPS can be effectively used as a specific extractant for silver in nitrate media.

Table 2

Effect of retention time (RT) on separation factor*

RT (min)	Ag/Cd	Ag/Cu	Ag/Fe	Ag/Pb	Ag/Zn	% Ag extr.
0.5	24×10^6	96×10^6	5×10^6	2×10^6	32×10^6	99.89
1.0	100×10^6	30×10^6	20×10^6	5×10^6	65×10^6	99.94
2.0	100×10^6	40×10^6	10×10^6	5×10^6	65×10^6	99.97
4.0	100×10^6	40×10^6	10×10^6	5×10^6	65×10^6	99.97
8.0	100×10^6	40×10^6	10×10^6	5×10^6	65×10^6	99.99
10.0	100×10^6	20×10^6	20×10^6	4×10^6	65×10^6	99.99

*A/O=1, T=24°C

Equilibrium and Maximum Loading

As we can see from the kinetic test the equilibrium is reached with 2 min. of contact. Extraction isotherms were obtained with two contact times, 0.5 and 10.0 min. and they were found to be almost identical. The results are summarized in Table 3 and Fig. 1.

Table 3

Effect of A/O ratios on silver extraction

A/O	D		% E	
	0.5 min	10.0 min	0.5 min	10.0 min
1/1	>900	9000	99.89	99.99
3/1	>10000	10000	99.99	99.99
5/1	>8000	8000	99.89	99.88
7/1	>500	500	99.81	99.80
10/1	35	32	77.02	75.00
1/3	3400	3400	99.99	99.99
1/5	2000	2000	99.99	99.99
1/7	1430	1430	99.99	99.99

These results show that the maximum loaded capacity of 3.5 $^{w}/_{o}$ TiBPS is about 7 kg/m^3. A maximum disengagement time of 5 min. was observed for the various ratios tested. Some emulsions and haziness were also observed. Therefore, to improve the physical separation characteristics, 5 $^{v}/_{o}$ of nonylphenol was used as a modifier. In this case shorter disengagement times were observed, less than 3 min, without significant haziness or emulsions. Disengagement time was found to increase with increasing A/O ratios with or without nonylphenol. The pH of the aqueous phase does not change after the reaction. The concentration of free NO_3^- ions is also unchanged. These results corroborate with previous findings with a type of compound similar to TiBPS. It was reported[19] that triphenylphosphine sulphide did not extract nitric acid when the HNO_3 concentration was low.

According to the above data the following reaction can be proposed for the extraction of silver with TiBPS:

$$AgNO_{3\,a} + 2TiBPS_o \rightarrow 2TiBPS \cdot AgNO_{3\,o}$$

These type of disolvated,, S→Ag←S, complexes are common among the compounds that silver forms with S-donor types of molecules[22,23]. A maximum loading capacity of TiBPS (3.5 $^{w}/_{o}$) calculated with the above equation confirms the experimentally found loading capacity of 7.0 kg/m^3 (7.4 kg/m^3 theoretical).

The extraction isotherm was also constructed using the technique of ten consecutive contacts of the same organic with fresh feed solution (A/O=1). Lower loading capacity of about 6.5 kg/m^3 of silver was found. Also in this series of tests an addition of 5 ^{v}/o of nonylphenol was found to significantly improve the physical characteristics of the system. Investigations are now under way to determine the factors responsible for these poor loading and separation characteristics when the consecutive contacts technique is applied. Nevertheless, selectivity did not suffer and similar separation factors to those in the case of one contact, were found.

TiBPS-Ag Complex

In order to clarify the proposed extraction mechanism, the complex of TiBPS with $AgNO_3$ was synthesized, and its properties were studied. Analytical and preliminary X-ray diffraction results[24] indicated that the complex is disolvated, a finding which confirms the extraction equation given previously. The spectroscopic results (IR, NMR) confirm the existance of a coordination bond between sulphur and silver. The P=S stretching frequency of TiBPS which is about 586 cm^{-I} was shifted to 560 cm^{-1}. This decrease corresponds to the weakened back-bonding ability of sulphur to phosphorus due to the formation of a Ag-S bond. The same was concluded from the ^{31}P NMR spectrum where a shift of about 6 ppm was observed in the frequency of P of TiBPS after complexation took place.

The isolated complex, $2TiBPS \cdot AgNO_3$, an off-white crystalline compound, was found to decompose slowly yielding a black powder. The decomposition was drastically retarded if the product was kept in the dark. This can be explained by the well known fact that silver compounds are light-sensitive. The complex, $2TiBPS \cdot AgNO_3$ was also found to decompose, in $CHCl_3$ and MeOH solutions. Very concentrated solutions were decomposed faster than dilute ones. The same was observed when commercial diluents were used, e.g., Solvesso 150, although the decomposition rate was much lower. Thus, highly loaded organics, about 7 kg/m^3, started decomposing after standing overnight, while diluted solutions (1 kg/m^3) were stable for several days.

Factors influencing the stability of the complex, e.g., solvent, concentration, light, temperature, are under investigation since crud or emulsion formation may possibly be related to these.

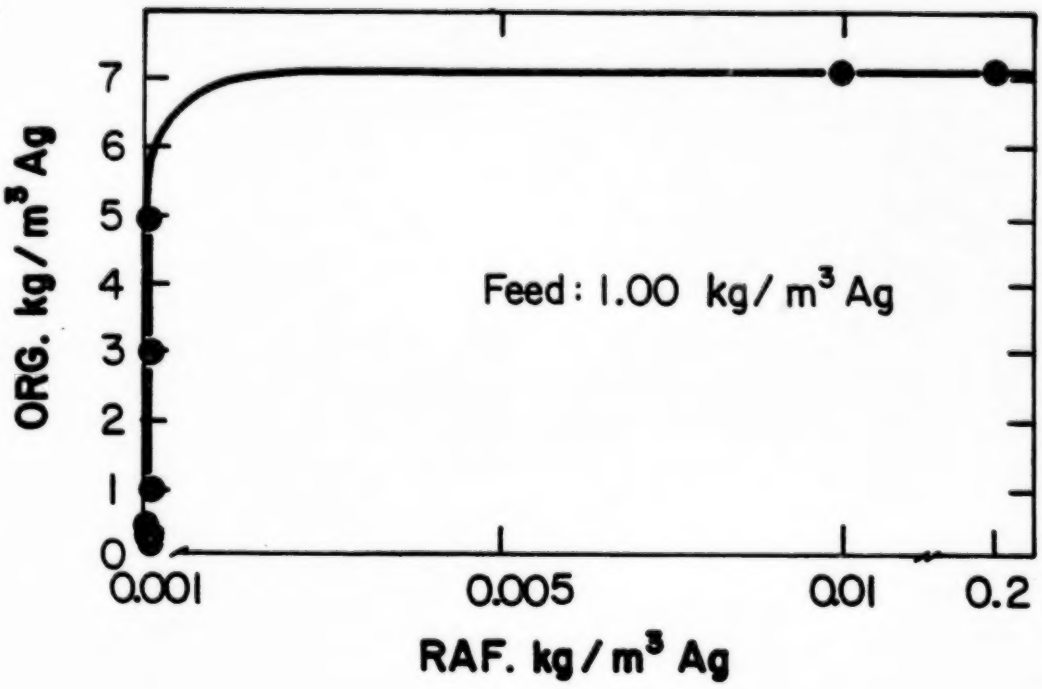


Fig. 1. Extraction isotherm (R.T. 10 min.)

Stripping Studies

In order to select a stripping agent, screening tests were performed with three possible agents, nitric acid, ammonium hydroxide and sodium thiosulphate. Stripping with HNO_3 was unsuccessful when concentrations of the acid varying from 1 to 30 $^{v}/o$ were tried.

Various concentrations of NH_4OH were tested from 1 to 25 $^{v}/o$. The optimum stripping was observed with 15 $^{v}/o$ solution. However, this stripping system was associated with some unattractive features. The disengagement times were in the range of 5 to 10 min. depending on the NH_4OH concentration. The organic phases always contained some black precipitate and were hazy while the strip solution was emulsified. Thus, no further work was conducted.

The most successful stripping agent was found to be sodium thiosulphate. The results (Table 4) indicate that silver can be almost completely recovered in a single stage with 5 min. retention time. Concentrations of 0.5 M and 1.0 M sodium thiosulphate gave equally satisfactory results.

Table 4

Effect of retention time (RT) and sodium thiosulphate molarity on stripping of loaded organic*

RT min	M	% stripped organic
5	0.5	98.02
5	1.0	96.02
10	0.5	99.25
10	1.0	99.04
15	0.5	97.00
15	1.0	98.54

*A/O=1, T=24°C

Although the nitric acid solutions are acceptable for the extraction of silver[25], this does not imply that we advocate the dissolution of silver-bearing materials in nitric acid for its subsequent recovery by TiBPS. Rather, it indicates a mechanism for extraction of silver and one could consider the treatment of high level silver compounds such as anode

slimes, Pb-Ag sulphate precipitates and possibly jarosites as feeds to a nitric acid-TiBPS circuit. Naturally the nitric acid would have to be recovered from such a circuit for recycle.

CONCLUSION

From the above results it becomes clear that TiBPS has an excellent selectivity for silver over other metals such as cadmium, copper, iron, lead and zinc, and the extraction of silver is almost complete (above 99%), from nitrate solution in less than 2 min. contact in a single stage. A disolvated complex, $2TiBPS \cdot AgNO_3$, was formed between TiBPS and $AgNO_3$ and this was isolated and identified. However, TiBPS was not a satisfactory silver extractant from highly concentrated chloride solutions (270 kg/m^3). Sodium thiosulphate appeared to be the best of the examined stripping agents, over NH_4OH, HNO_3, with nearly total recovery of silver from the loaded organic.

The excellent selectivity and extraction ability (from nitrate solution), is masked by some difficulties dealing with the stability of the TiBPS-Ag species, formation of emulsions etc. Although a 5 $^v/_o$ addition of nonylphenol had improved the situation more studies are now in progress in order to determine the reasons for the above mentioned difficulties.

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REFERENCES

1. Seeley, F.G. and Crouse D.J., J. Chem. Eng. Data 11, 424 (1966).
2. a. Chernyak, A.S., Skobeev, I.K., Bobrova, A.S. and Ivanov, O.P., Tsvet. Met. (4), 24 (1967),
   b. Selmer-Olsen, A.R., Acta Chem. Scand. 20, 1621 (1966).
3. Irving, H.M. and Damoran, A.D., Anal. Chim. Acta 53, 267 (1971).
4. Hayliem, D. and Zangen, M. in Solvent Extraction Conference ISEC 77 Vol. 1, 107 (1977).
5. Sekine, T. and Hasegawa, Y. in "Solvent Extraction Chemistry"; Dekker 1977, 609.
6. Levin, V.I. and Kozlova, M.D., Radiokhimiya 8, 533 (1966).
7. Miranov, V.E. and Lastovkina, N.P., Zh. Neorg. Khim. 10, 1082 (1965).
8. Hala, J., J. Inorg. Nucl. Chem. 27, 2659 (1965).
9. Pearson, R.G., J. Am. Chem. Soc. 85, 3533 (1963).
10. Mikhailov, H.W. and Torgov, E.N. in Solvent Extraction Conference ISEC 1971, Vol. 2, 1112 (1971).
11. Mikhailov, H.W. in Solvent Extraction Conference ISEC 77, Vol. 1, 52 (1977).
12. Handley, T.H. and Dean, J.A., Anal. Chem. 32, 1878 (1960).
13. Handley, T.H., Anal. Chem. 35, 991 (1963).
14. Handley, T.H. and Dean, J.A., Anal. Chem. 34, 1312 (1962).
15. Bode, H. and Arnswald, W., Z. Anal. Chem. 185, 179 (1962).
16. Levin, I.S., Sergeeva, V.V., Tarasova, V.A., Varentsova, V.I., Rodina, T.F., Vorsina, I.A., Kozlova, N.E. and Kogan, B.I., Zh. Neorg. Khim. 18, 867 (1973).
17. Elliott, D.E. and Banks, C.V., Anal. Chim. Acta 33 237 (1965).
18. Hitchcock, R.B., Dean, J.A. and Handley, T.H., Anal. Chem. 35, 254 (1963).
19. Cattrall, R.W., Martin, A.R. and Tribuzio, S., J. Inorg, Nucl. Chem. 40, 687 (1978).
20. Blednov, B.P., Letuchaya, V.A., Borbat, V.F., Drovnikova, Z.I., Kouba, E.F., Bekenova, V.N., Smorodnikova, L.L. and Pavlenko, A.F., Nauchn. Tr. Sib. Gos. Nauchno-Issled Proektn. Inst. Tsvetn. Metall. (6), 182 (1973), [CA 81, 156442d (74)].
21. Van der Veer, W. and Jellinek, F., Rec. Trav. Chim. Pays-Bas 85, 842 (1960).

22. Marsicano, F. and Hancock, R.D., J. Coord. Chem. 6, 21 (1976).

23. Torgov, V.G., Shatskaya, S.S., Galtsova, E.A., Yumatov, V.D. and Mazalov, L.N., Tezisy Dokl.-Vses. Soveshch. Khim. Anal. Tekhnol. Blagosodn. Met. 10th 1, 68 (1976), [CA 90, 29842v (79)].

24. Szymanski, J., CANMET, Crystallography Section, Personal Communication.

25. Hoh, Y.C., Chang, C.C., Chuang, W.S., Lee, B.D., Tai, J.J., Feng, W.L., Ma, T., Ko, C.S., Chen, W.L., Wei, T.Y., Liu, L.C. and Wang, W.K., Proc., 3rd International Symposium on Hydrometallurgy (Atlanta 1983) 151, (1982).